

## Thermal, spectroscopic and electrical transport properties of processable poly(aniline-co-alkylaniline) copolymers

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Aniline has been copolymerized in the presence of substituted anilines as comonomers to prepare conducting copolymers of poly(aniline-co-alkylaniline) type, via the chemical oxidative polymerization route. Their thermal stabilities and conductivities are slightly less than pure polyaniline but processabilities have been improved significantly. These copolymers exhibit improved solubility in organic solvents like 1-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), and dimethyl formamide (DMF). Conduction mechanism has been found to be 3-D VRH in case of pure HCl-doped polyaniline and 1-D VRH for copolymers. Coating of these polymers on insulating surfaces can be used for ESD protection and corrosion prevention of iron and mild steel under hostile conditions.

**Keywords:** Polyaniline, Copolymers, Variable range hopping (VRH), Poly(aniline-co-isopropyl aniline), Poly (aniline-co-2-secbutyl aniline), Conductivity, TGA, FTIR, XRD.

In the recent years, conducting polymers have become center of gravity of polymer and material science due to their novel electronic and electrical properties. These polymers have diverse applications ranging from energy storage<sup>1,2</sup>, sensors<sup>3-5</sup>, anticorrosive materials<sup>6-8</sup>, electromagnetic interference shielding<sup>9-11</sup>, electrostatic charge dissipation<sup>12-14</sup>, organic light emitting diodes<sup>15-18</sup>, plastic solar cells<sup>19,20</sup> and supporting material for catalysis<sup>21,22</sup>. However, among other conducting polymers, polyaniline has been extensively studied, not only because its electronic conductivity can easily be tuned by adjusting the oxidation state and degree of doping of the backbone, but also due to its environmental stability as well as economic feasibility. Therefore, polyaniline is a promising futuristic material for various techno commercial applications.

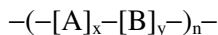
Polyaniline is made up of combination of fully reduced (B-NH-B-NH) and fully oxidized (B-N=Q=N-) repeating units, where B denotes a benzenoid and Q denotes a quinoid ring. Thus, different ratios of these fully reduced and fully oxidized units yield various forms of polyaniline, such as leucoemeraldine (100% reduced form), emeraldine base

(50% oxidized form) and pernigraniline (fully oxidized form). However, all of these forms are electrically insulating in nature. Doping of emeraldine base with a protonic acid converts it into conducting form protonated emeraldine (emeraldine salt). The main issue with polyaniline is processing difficulties due to its infusibility and relative insolubility in common organic solvents. It can be made processable/soluble either by polymerizing functionalized anilines<sup>23,24</sup> or by copolymerising aniline with substituted monomers<sup>25-27</sup>. Bulky counter-ion induced processability<sup>28,29</sup> has also been reported by several groups. Electronic properties of these synthetic metals can be tailored by carrying out the polymerization under the controlled conditions and in the presence of specific dopants.

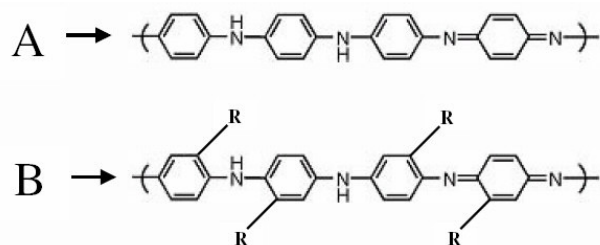
In this paper, the copolymerization of aniline in the presence of alkylaniline as comonomers to prepare conducting copolymers of poly(aniline-co-alkylaniline) type via the chemical oxidative polymerization route has been reported. These copolymers are characterized by the various techniques like TGA, UV-Visible spectroscopy and FTIR. Their electronic conductivities have been measured by four-probe technique. VRH model has been applied depending upon the nature of variation of conductivity with temperature.

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Considering the four-unit repeat structure, these copolymers can be represented by the following general formula:



where,



Here “A” and “B” are blocks of poly(aniline) and poly(alkylaniline) respectively and “n” is average degree of polymerization. The block lengths “x” and “y” depends upon the nature and size of the alkyl substituent as well as on the polymerization conditions (pH, temperature, reaction medium and inert atmosphere). The same factors also govern the value “n” and low temperatures favors high values of “n”.

## Experimental Procedure

### Materials

Aniline (Loba Chemie), 2-methylaniline (Merck), 2-ethylaniline (Aldrich), 2-isopropylaniline (Acros Organics), 2-secbutylaniline (Aldrich), HCl (35.4% s.d fine-chem), and Ammonium peroxydisulfate (APS, Merck) were used without further purification. Liq  $\text{NH}_3$  (30%, Loba Chemie) was used to dedope the doped polymers. NMP (Merck), DMF (Qualigens), DMSO (Qualigens) and Acetone (Merck) were used for making solutions. Aqueous solutions were prepared from the double distilled water having specific resistivity of 1  $\text{M}\Omega\text{-cm}$ .

### Polymerization

The doped polyaniline substituted polyaniline and their processable copolymers were chemically prepared by free radical oxidative polymerization route. The concentration of both of aniline and substituted-aniline was 0.1 M and that of HCl was 1.0 M. For the copolymer, aniline and substituted aniline were mixed in the mole ratio 95:5. Polymerization was initiated by the drop wise addition of ammonium peroxydisulfate (0.1 M,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in 100 mL  $\text{H}_2\text{O}$ ). The polymerization was carried out at a temperature of  $-5.0 \pm 1.0^\circ\text{C}$  and over a period of 4-6 h. Then the

doped polymer powders were obtained by the processes of precipitation, filtration, rinsing and drying, successively. The above-synthesized powders were treated with 0.1 M aqueous ammonia and stirred for 2 h to obtain their base (undoped) forms. In the present work, we have deliberately kept the concentration of alkyaniline in the copolymer low in order to maintain a optimum combination of solubility and conductivity. The names of different homopolymers and their respective copolymers have been abbreviated by the specific codes taking into account the comonomer feed ratios. For example CP100 means 100% pure polyaniline (homopolymer). CP95Mt means a copolymer having molar ratio of aniline to methylaniline as 95:5 in the comonomer feed. Similarly CP95IP means a copolymer having molar ratio of aniline to isopropyl aniline as 95:5. These abbreviations are given in Table 1 and the same code has been used throughout the rest of the paper.

### Measurements

For the conductivity measurements, pellets of length 13 mm, width 7 mm, thickness 1-2 mm were prepared and the resistivities were measured by four-point probe technique using (Keithley 220 Programmable Current Source and 181 Nanovoltmeter). TGA (Mettler Toledo TGA/SDTA 851 $^\circ$ ) was used to observe the thermal behaviour. Materials were heated from 25 to 700 $^\circ\text{C}$  under a constant heating rate of 10 $^\circ\text{C}/\text{min}$ , in the inert atmosphere of nitrogen. The samples were also studied by using UV-visible spectrophotometer (Shimadzu UV-1601) after preparing solutions of their base forms in NMP, and DMF and doped forms in MEG. FTIR (NICOLET 5700) and XRD (D8 Advance Bruker AXS X-ray diffractometer) were used to observe the characteristic peaks of these copolymers. Micromorphology was observed using SEM (Leo 440, UK). Solubilities were recorded at room temperature on the basis of pass through a 0.45-micron filter.

## Results and Discussion

### Polymerization mechanism

The polymerization of aniline and copolymers proceeds via a typical free radical oxidative polymerization route. The main steps are involved in the process are:

#### Initiation

Initiation was effected by  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (APS), which generates the free radicals. These under the

Table 1—Abbreviations, electrical, chemical and spectroscopic attributes of the materials

Polymer	Abbreviation	Conductivity (S/cm)	UV-Visible bands in NMP $\lambda$ (nm)	FTIR bands Wavenumber ( $\text{cm}^{-1}$ )	Solubility (g/L)
Homopolymer (100% aniline)	CP100A	25.6	329 638	799,1123,1243,1298, 1399,1497,1577	0.9
Copolymer (Aniline:Methyl-aniline::95:5)	CP95Mt	13.5	328 630	796,1103,1240,1296, 1397,1468,1556	4.3
Copolymer (Aniline:Ethyl-aniline::95:5)	CP95Et	11.2	327 629	799,1123,1242,1300, 1401,1473,1558	5.5
Copolymer (Aniline:Isopropyl-aniline::95:5)	CP95Ip	12.8	326 630	798,1105,1241,1298, 1397,1474,1560	4.3
Copolymer (Aniline:Secbutyl-aniline::95:5)	CP95Sb	4.7	326 631	796,1105,1239,1295, 1399,1473,1577	2.3
Homopolymer (100% Methyl-aniline)	CP100Mt	0.45	317 613	758,1108,1183,1268, 1389,1462,1559	8.5
Homopolymer (100% Ethyl-aniline)	CP100Et	0.06	314 618	756,1112,1154,1274, 1378,1490,1588	11.8
Homopolymer (100% Isopropyl-aniline)	CP100Ip	$\sim 10^{-4}$	306 506	755,1145,1192,1263, 1384,1465,1576	22.4
Homopolymer (100% Secbutyl-aniline)	CP100Sb	$\sim 10^{-5}$	302 515	756,1130,1175,1268, 1382,1458,1565	24.8

proper pH conditions react with aniline monomer to form radical cations. However, the radical cations are resonance stabilized and can be represented by various canonical forms.<sup>30</sup>

#### Propagation

Propagation step involves the addition of radical cations to oligomeric species to form polymeric chains. Each radical cation has two active sites that may be attributed to the increased electron density at ortho and para positions of benzene ring. However, coupling of radicals depends upon several factors including reaction medium, temperature, pH and presence of bulky substituents. Therefore, due to the steric hindrance offered by the  $-\text{NH}_2$  group, ortho coupling has almost been excluded leading to the formation of para product. However some ortho coupling<sup>31</sup> also occurs leading to the formation of corrupted polymer. Chain growth continued till it is arrested either by chain transfer or by coupling of radicals. Low temperature favours the formation of long chains (high molecular weights) due to the retardation of the rate of termination and chain transfer reactions.

#### Termination

Termination occurs due to the exclusion of radicals either due to coupling or by disproportionation reaction.

The copolymerization is a powerful method to improve processability of conducting polymers. In general solubility of substituted-polyanilines in organic solvents is significantly higher than pure polyaniline. However, their thermal stability and electronic conductivities are substantially lower than doped polyaniline. In order to maintain balance between conductivity, stability and processability copolymerization has been done. However, the relative proportions of aniline and substituted aniline in the copolymer determine exact properties.

#### Conductivity

Figures 1a and 1b show the variation of conductivities of doped CP100A and CP95Ip with temperature in the range 50-300 K. As can be viewed, conductivity of both the samples increases exponentially with the temperature. The same trend has been observed in other copolymers too. This shows that these copolymers obey temperature dependence of conductivity similar to conventional semiconductors. From Figs 1a and 1b, the room temperature conductivities of doped CP100A and CP95Ip are found to be 25.6 and 12.8 S/cm respectively.

We have also tried to fit the appropriate model for the variation of conductivity of the materials with temperature, in the temperature range 25-300 K. For

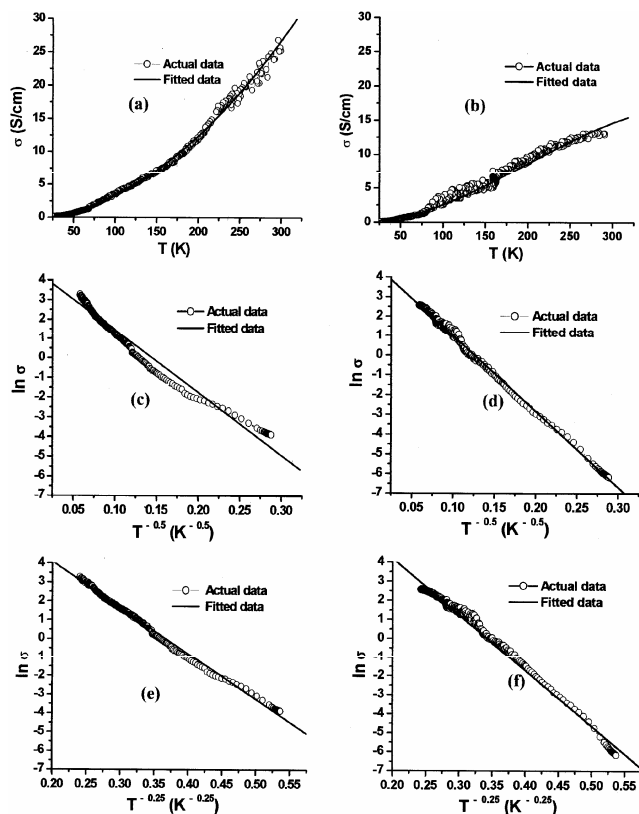


Fig. 1—Plots of d.c. conductivities ( $\sigma$ ) versus temperature ( $T$ ),  $\ln \sigma$  versus  $T^{1/2}$  and  $\ln \sigma$  versus  $T^{1/4}$  for doped polymers (a), (c), (e) CP100A and (b), (d), (f) CP95Ip respectively.

the above models we have considered that samples follow the VRH model<sup>32-35</sup>. In the VRH regime, temperature dependence of conductivity ( $\sigma$ ) follows the generalized relation.

$$\sigma = \sigma_0 [\exp -(T_0/T)^{1/r}]$$

where  $T_0$  is the Mott characteristic temperature and is a measure of the hopping barrier. The  $\sigma_0$  is conductivity at infinite temperature. Their values are determined by density of states, localization length and average hopping distance. The value of  $r$  is related to the dimensionality ( $d$ ) of the system as  $r = (d+1)$ . For the one, two and three-dimensional systems,  $d$  is equal to 1, 2 and 3 respectively and corresponding values of  $r$  are 2, 3 and 4 respectively.

Figures 1c and 1d show the variation of conductivities of doped CP100A and CP95Ip when plotted as  $\ln \sigma$  versus  $T^{1/2}$ . On the other hand, Figs 1e and 1f show the variation of conductivities of the same materials when plotted as  $\ln \sigma$  versus  $T^{1/4}$ . As can be seen from Figs 1c and 1e, for the HCl doped CP100A, linear dependence of  $\ln \sigma$  on  $T^{-0.25}$  is better

than that of  $\ln \sigma$  on  $T^{-0.5}$ . The former has a linearity fit factor of 0.99765 whereas the latter has that of 0.98494. Therefore, 3D-VRH ( $r=4$ ) model suits better for doped CP100A. These findings are consistent with reported by Li *et al.*<sup>35</sup>. Therefore, for CP100A the value of  $T_0$  evaluated from the slope of the straight line of the Fig. 1e is 452075 K. The corresponding value of  $\sigma_0$  is 13542 S/cm. On the other hand, Figs 1d and 1f reveal that for the HCl doped copolymer (CP95Ip) the linear dependence of  $\ln \sigma$  on  $T^{1/2}$  is better than that of  $\ln \sigma$  on  $T^{1/4}$ . The linearity fit factors for the plots of  $\ln \sigma$  versus  $T^{-0.25}$  and  $\ln \sigma$  versus  $T^{-0.5}$  are found to be 0.99463 and 0.99806 respectively. Thus 1D-VRH seems to appropriate model for the doped CP95Ip. Other copolymers have also shown behaviour similar to CP95Ip, i.e., 1-D VRH. For the doped CP95Ip, the values of  $T_0$  and  $\sigma_0$  from straight line of Fig. 1c are 1533 K and 145 S/cm respectively.

In case of HCl doped CP100A  $\text{Cl}^-$  ions are small and the interchain separation is small, resulting in appreciable coupling interactions between the chains. Thus, charge carriers could easily hop from one chain to other to give of 3D-VRH conduction. Besides that charge carriers could also hop between granular particles as 3D-VRH. However in the case of copolymers although the charge carriers hop between granular particles as 3D-VRH but interchain hopping has been strongly inhibited leading to 1D-VRH. The reduction in interchain hopping may be attributed to the presence of bulky alkyl groups in the copolymers that reduces the coupling interactions between the chains. Therefore, the net effect is the 1-D VRH conduction in case of all copolymers.

Table 1 shows the room temperature conductivities of the doped samples. Conductivity data clearly shows that the copolymers are less conducting relative to the polyaniline. The conductivity decreases both due to decrease in conjugation length as well as less doping level achieved.

#### SEM studies

Figure 2 shows the SEM micrographs of the doped CP100A and CP95Ip respectively at different magnifications. Figures 2a and 2b show low magnification (2KX) micrographs and indicate the presence of globular morphologies in both CP100A and CP95Ip. These globular particles consist of large